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Variation with time of the current in an ozonizer contraction (discharge) under d. c. excitation

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The count rate in Siemen ozonizer type tubes filled with dry air at various low pressures, as measured by direct current impulse potential passing through it, has been found to decrease with the time during which the discharge is maintained reaching eventually a minimum value. It is concluded that this decrease is due to species formed during the discharge and adsorbed on the glass surface. It is also concluded that the ionization in the gaseous phase is small, and that the count rate occurs by a sudden release of a cascade of electrons from the cathode, these electrons being responsible for decay formation through an air-atom mechanism.

1. INTRODUCTION

Earlier results of Joshi and co-worker on the time variation of new light effect in a number of gases (Joshi 1939, 1944, 1945, Deo 1945), the marked influence of traces of impurities and the wall effect in electrically excited systems (Joshi 1943, 1945, Rao 1945) have revealed that the nature of the electrode surface (Joshi 1944, 1946a, 1946b) represents an important determinant of the eigate-effect (light effect).

Most of the data available in the literature on the Siemen-type ozonizer processes were based on current intensity and energy consumption measurements using (a) a thermal junction and galvanometer, (b) a quadrant electrometer (Warburg 1909, 1923, 1925) and other meters sensitive to low frequencies. It was of interest, therefore, to investigate the possible contribution of sorbed gases in the observed decay of the discharge rate with an electronic scaler (SS 361 A, Atomic Energy Establishment, Trombay, Bombay) under d.c. excitation.

2. EXPERIMENTAL

Most of the experiments were done with glass-ozonizers. The two ozonizers of different inter-electrode spacing and various volumes of the space compartments were selected in the present work. For this investigation on air, the inner and outer spaces were filled with dilute electrolytic solution (NaCl). The middle space of both the ozonizers filled with dry air at 1 and 10 mm of

mercury pressure. The two columns filled with salt solution served as the two electrodes of a discharge tube. They were connected to study potential of 1500 V to excite the discharge (figure 1) and the current was measured with a scaler. The experiments were done in a wooden box at room temperature (27°C) and at 165°C and external light was completely excluded in order to avoid photo-induced effects (Joshi 1943, Ramaiah 1961).

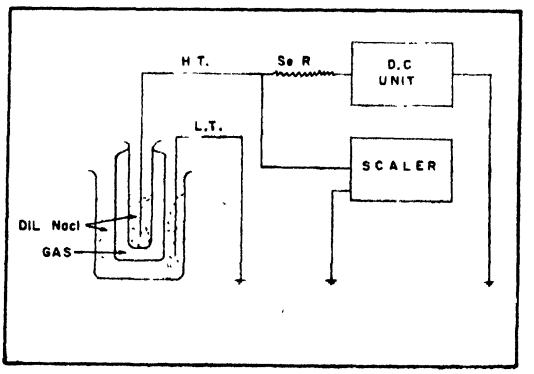

Fig. 1. Circuit for the study of the effect of time on discharge pulses in air.

3. The Current-Time Relationships Occuring in an Ozonizer or Ionizing Vessel

The problem is conveniently restricted to the standardized type of vessel consisting essentially of two concentric glass or quartz tubes, the outer surface of the outer tube and the inner surface of the inner tube being arranged to serve as electrodes.

This arrangement constitutes a system of three condensers in series : the condenser C_{iw} of the inner wall, the capacitance C_{ga} between the inner surface of the outer tube and the outer surface of the inner tube, i.e., annular space filled with air, and the capacitor C_{ow} of the outer wall. It may, therefore, be represented in the conventional symbols, such as C_{iw}, C_{ga} and C_{ow}, where it is assumed that for all practical purposes the power factor of C_{iw} and C_{ow} are negligibly small.

The insulating power of glass is much higher than that of the gas under the same condition. It follows, therefore, that at a certain potential the condenser C_{ga} due to gas (air) begins to leak due to ionization in the gas. The condensers C_{iw} and C_{ow} comparatively do not leak as the dielectric strength of glass is greater than that of the gas. When, therefore, the gas just begins to ionize at the first threshold potential, the gas capacitor C_{ga} is shunted by a fictitous resistance, which is equal to the reciprocal of the current which flows through the gas.

The direction of the current in an ozonizer discharge is at right angle to the axis of the annular space, or better still it is at right angle to the length of the gas gap. It follows, therefore, that all positive ions which start from inner electrode (anode) to outer electrode (cathode) will be stopped by the glass walls so also all the negative ions which start from the outer electrode and move towards the inner electrode will be stopped completely by the glass wall.

3.1 Determination of Small Elementary Area

$$q = C\delta V_A.$$

where δV is the surge voltage, diminution in voltage on the glass electrode due to the impact of the avalanche: q is the charge associated with an individual pulse and C is the capacitance of the wall material. This equation was used by Manson (1959) for finding out the charge associated with a pulse related with the capacitance of the wall material. From this relation, Kanitkar (1967) has recently not only obtained the value of the capacitor C, but also determined the site area or small elementary area. This capacitance and the average site area estimated was about 3·12 pf and 0·76 cm^2 respectively. This average small elementary area is in good agreement with the value (1 cm^2) obtained by Harries & Von Engel (1951).

4. Results

At a constant applied V, under a.c. or d.c. applied to the system containing an unreactive gas, it is expected from the general physical theory (in Fleming valve's thermionic characteristics, the values of the current remain constant with time at a constant potential) that the current I should be constant. It has been observed, however, in case of an ozonizer that the current as measured by scaler varied with time, although the applied V was constant and the gas used was low pressure air. It is of interest, therefore, to investigate the possible cause or causes responsible for this time variation of the current.

At a constant 1500 V.d.c., 5 V. and 50 V discriminator bias and room temperature (27°C), the table 1 shows that during the initial stage, the count rate per three minutes in a perfect dark wooden box increases with time from an initial 173 to about 200 in two hours and thereafter it decreases nearly to zero in about 13½ hours. After 24 hours rest, on repetition at 50 V disc. bias C_D/3 min. decreases progressively to almost zero with 7½ hours of continuous discharge, from 9.30 to 17.00 hours (figure 2).

The results in figure 3 show that at 1500 V. d.c.; 50 V disc. bias and 165°C, the counts per two minutes under dark illumination in air-ozonizer at 10 mm decrease continuously without any fluctuation from an initial of about 26,500 to a minimum of about zero in one hour only. A comparison of the results of

the three series of experiments, namely figures 2 and 3, shows that the presence of 10 mm Hg of pressure of air in an annular space, a pulsed emission decay is the greatest in a very short continuous duration of discharge at 165°C and 50 V discriminator bias (figure 3). The average charge on each small elementary area would decrease, assuming that the charge density on the walls remains unaltered, at a given applied V. The continuous duration of discharge would, therefore, be of shorter in time as compareed to those obtained with the fresh tube.

Table 1. Variation of current with time.

Applied Potential	:	1500 V. d.c.
Pressure of Air	:	1 mm Hg.
Temperature of the system	:	27°C
Pulse Height	:	50 V.
Current Indicator	:	S. 361, A. Scaler.

(Annular surface coated with NaCl in H_2O Solution)

Fresh Ozonizer;Tube No. 1

Time (minutes) T_m	C_D/3 min. in arbitrary units	Time (minutes) T_m	C_D/3 min. in arbitrary units
0	173	510	27
30	174	540	26
		570	20
60	173	600	15
90	187	630	11
120	202	660	4
150	195	690	6
180	187	720	9
210	177	750	10
240	172	780	7
270	156		
360	65	810	1
390	63	840	1
450	42	870	0
480	41	900	0

5. Influence of Temperature on Discharge Counts

A series of experiments were made to study the effect of the variation of temperature on the magnitude of the discharge counts in dark. One of the typical groups of results obtained by increasing the temperature of the electrolyte from 27°C to 165°C is given in table 1 and figure 3. It is seen that at a given applied V and discriminator bias, C_D increases with the temperature. Thus, e.g., at 1500 V. d.c., 50 V disc. bias, the initial and final values obtained for C per minute

at 27°C and 165°C were about 57, 13.250; and 0, 1 respectively. It is quite possible that under heavy electrical discharge during continuous aging at high temperatures, admixture of gases are dissociated and is readily sorbed by glass walls of the discharge tube. Excited molecules and atoms of diatomic gases in air, compounds such as water vapour, formed under electrical discharge may also be deposited on the surface of the glass walls. Thus, in effect, the poisitive and negative electrode-surfaces are coated with a surface layer consisting of atoms and molecules when the tube is operated at high temperature and continuous aging. As suggested by Joshi (1943, 1945, 1947) and some other investigators (Rao 1948, Arnikar 1952), this layer possesses a low work function making photo-electric emission possible. It is probably on account of formation of the boundary layers and the reduction in the site area that the contraction tube is sensitized due to continuous aging and operation at high temperatures for the production of current emission decay.

As explained above, the total number of small elementary area in a high temperature increases as a result of the decrease in area of the sites under a steady potential, as the total area on the electrode wall is constant. Because of this, an increase in the total number of counts in dark in the discharge processes can be expected.

6. Count Rate-Time Characteristics

The decay of the discharge current with time in minutes in air-ozonizers at low pressures such as 1 and 10 mm. Hg. are plotted in figures 2 and 3 respectively. It is seen in figure 2 that the count rate in a given time increases from the initial value to a peak point A. It also shows that the curve has two marked peaks. A first marked peak, denoted by A, is formed at low values of time beyond which $C_D/3$ min. diminishes, as time increases up to 660 minutes. Further increase in time shows a second marked peak at high values of time, T_m, (750 minutes) and thereafter the C_D reaches to zero with time.

Aging effect (Joshi, 1939, 1943, 1944, 1945, Deo 1945, Geol 1947, Mallikarjunappa 1948, Kanitka 1967) has also been studied under d.c. discharge at a constant gas pressure, such as 1 mm, (*i.e.*, in the former the discharge tube was kept excited at a fixed potential, 1500 V. d.c., for 30 hours and in latter the opposite process as the system was stood over in the absence of discharge, unexcited in the rest period 24½ hours). The influence of aging for 30 hours at a typical pressure produces a rapid decrease in counts from 164 to 0 (figure 2: curve no. II). This remarkable effect, when compared with the observations taken in the fresh gas (table 1, figure 2, curve I), does not show any similarity This, therefore, indicates that aging produces a deposit of impurities on the walls of the ozonizer and thus the electrode surface seems to be permanently poisoned. A similar observation is reported in SO_2 and CO by Deshmukh & Dhar (1949), Deshpande (1963) respectively.

In curve No. I of figure 2, the point A represents the beginning of the sudden discharge current collapse. C_D/3 min. collapses suddenly in a time of the order of about 240 minutes, after which a more or less pronounced step may or may not be in evidence. By about 660 minutes, the C_D per minute in figure 2, is about 1·4 and thereafter a steady state is gradually approached.

Figure 3. Count rate-time characteristic for 50 V Pulse height in air at a pressure of 10 mm Hg, showing the effect of temperature (165°C) on a pulsed emission decay in tube No. 2.

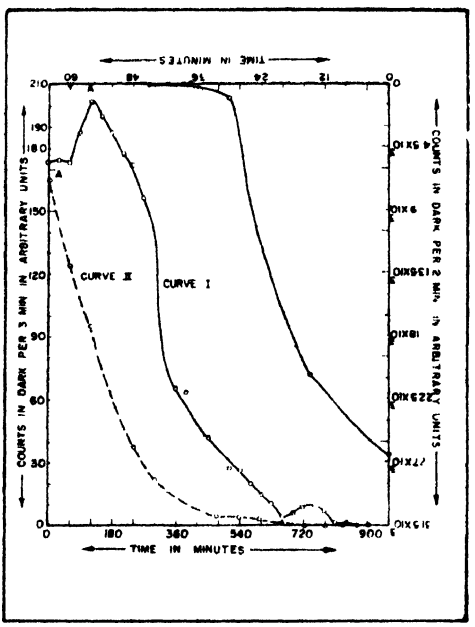

Figure 2. Discharge rate in air at 1 mm. Hg. as a function of time for 50 V discriminator bias, showing the pulsed emission decay at a constant potential (1500 V d.c.) and room temperature (27°C). Solid curve-I for fresh and dashed curve-II for aged tube No. 1.

Figure 3 gives the count rate in dark per two minutes as a function of time. The experiments were done in a closed ozonizer filled with dry air at 10 mm pressure. Figure 3 shows that there is also a decrease in discharge rate. A similar decay (pulsed emission decay) effect has been observed in an electrodeless hydrogen discharge (John *et al* 1951) by the other techniques (Holt *et al* 1950). The current in figures 2 and 3 is given in arbitrary units. The ozonizer discharge system in air at a moderate pressure has only given a pulsed emission decay characteristics as illustrated in figures 2 and 3. It is instructive to note that the other electrode (cathode) formed by sleeves does not show the count rate emission decay phenomena in the same operating conditions. The observations

in ozonizer discharge eliminate possibility that the decrease of the discharge rate in air at 1 and 10 mm Hg. pressure is due to the electrical circuit, and more specifically to such effects as polarization of the glass dielectric, effects originating in the sodium chloride solution of the electrodes, etc.

The main general features of these curves are : (1) The usual vagaries of surface emitters here caused more than the usual error in measuring the count rate, since near about 120 minutes were required to obtain the decay characteristic at room temperature (as contrasted with the few minutes required to read a scaler). (2) The initial current increases as the size of the oxide or deposited particles on the surface of the walls decreases. (3) The count rate emission depends markedly on the treatment of surface of walls for the time just preceeding measurements. (4) Aged tube exhibited less range of decay than other fresh tube no. 1. This is probably due to a more activation of the negative electrode surface. (5) Comparison of figure 2 and figure 3 indicates that the same composition films produced differed decay range especially in figure 2. A probable cause for this is that the count rate decay with time may be proportional to the thickness of the particles composing the negative electrode surface. Benjamin, *et al* (1938) investigated the dependence of the thermionic current upon size of oxide particles and found an increase in steady state current with decreasing particle size. (6) In tube no. 2, the pulses show a more marked dependence on various factors; such as, pressure of dry air, inter-electrode spacing, temperature than exhibited by other tube (1), which suggests that the negative electrode surface in this tube may have been incompletely activated. (7) The positive space charge acts to decrease the inner electrode field (anode) and increase the outer electrode field (cathode field). Under these conditions, there is a strong fluctuation at constant applied field strength, say 1500 V.d.c., by causing extinction or intermittence of discharge. After a sequence of such interrupted discharges, the accumulated space charge in the low field regions reduces the effective field at the inner electrode so that discharge counts cease giving negative slope of current—time curve, *i.e.*, a pulsed emission decay, until virtually all the space charges clear from the annular space of the ozonizer in the clearing time interval. (8) In addition, there are several time effects of a few minutes or few seconds duration : Joule heating, poisoning of negative electrode by gas liberated from the positive electrode and a decay effect investigated by Blewette (1939). (9) The pulsed emission decay or count rate emission decay is of faster rate in an aged discharge tube at normal operating temperature as compared to those obtained with a fresh tube (Curve II of figure 2.)

7. Chemiluminescence

The more energetic species, *like ozone, and atomic oxygen,* can form the chemiluminescence. In the present experiments, the electrodes are surrounded

with an electrolyte. If these electrodes had been exposed for some time to discharge, a strong chemiluminescence may be formed. This chemiluminescence is obviously caused by the species formed during the dishcharge and adsorbed on the surface. By using air, the surface can be activated under discharge to cause chemiluminescence.

Since some electrical circuit is used to operate both the inner and outer electrodes, the elimination of the electrical characteristics of the circuit as being responsible for the decrease in the count rate is justified. This remarkable point gives the additional support that the surface species are responsible for the observed decay in discharge pulses. A possible explanation for this is that the formation of number of species on the electrode surface is maximum at the initial continuous aging, as the total area on the electrode wall is constant. This initial maximum total number of species decreases with time.

8. Discussion

Meek & Craggs (1953) have estimated the average electron energy for a given field strength, temperature, and pressure. At higher temperatures, molecules on the surface may undergo chemical change and thus be held by valence forces. The heat of adsorption is then far greater than corresponds to van-der Waal's adsorption. Such adsorption does not occur at low temperatures and in it the reaction velocity of the chemical change may be too low. Since there is an activation energy associated with each such a reaction, Taylor (1931) has proposed the term activated adsorption for the adsorption which involves such a chemical change. The distinction between van-dar-Waal's adsorption and activated adsorption was pointed out by Soderbaum in 1918 and illustrated by the adsorption of CO and of O_2 on platinum.

It was found (Deshmukh 1949) that the formation of the adsorption layer becomes noticeable above threshold potential of the gas, and it has been suggested that the initial step for the formation of adsorption on the glass walls is formation of positive and negative ions, radicals.

In this work, the applied potential (above starting potential) is large, and a still large voltage will be effective in ionizing gas. In the ozonizer, we do not have an external source of electrons. Moreover, the discharge pulses or ionization, under the same applied voltage, is more extensive in air at 10 mm and 165°C than it is in the same air at 1 mm of mercury pressure, 27°C.

According to Ramaiah (1959), the walls of the ozonizer are an insulator, easily removable electrons are not available, and the production of the electrons must be closely related to the gas adsorbed on the surface. Ionization of the gas must then be much easier in the adsorbed state than in the gaseous phase.

The ions formed remain in or near the glass surface. Our experiments with the ozonizer can lead to the same conclusion for the species responsible for the decrease in count rate. The mechanism of sudden release of a cascade of negative ions (electrons) from the outer electrode is not obvious to us, and we are extending our investigation in the hope of getting some information on this question.

The nature of species responsible for the decrease in discharge counts is not possible to deduce from our results. Some of its properties, however, can be described. The possible explanation for the decay in count rate with time growth is given that the species formed in air, and responsible for the decrease in pulses, are formed in the ozonizer discharge. The possibility that the species formed in dry air at 10 mm, 165°C are also formed (but less sufficiently) in the same gas at 1 mm of mercury pressure should also be considered. Deshmukh (1949) has already shown that there is a profound influence of the surface phenomena on the production of discharge current. It is observed that the rate of decay of the counts in the ozonizer discharge is very sensitive to the state of the (cathode) surface, and it is proposed that under the prevailing conditions the discharge takes place extensively on the surface. The factors such as increased temperature, electron impact, surface effect, etc. vary the discharge count rate in the electrodeless discharge.

9. Conclusions and Future Outlook

In this investigation, the decay of discharge count rate in dark with the time is seen in most of the air-ozonizers at constant potential 1500 V. d.c., discriminator bias 50 V and temperature of the system. The decrease in discharge counts is due to a decrease in the rate of initiation of the discharge at the outer electrode rather than to inhibition of the propagation. However, in light of above results, a possible explanation is that the species formed during the discharge are adsorbed on the surface of the walls and decrease the probability of the initiation of the individual discharges. This surface species are formed faster when the temperature of the system is high enough.

A comprehensive investigation has also been made for pulsed emission decay using the ozonizer tubes of different dimensions under various time and temperature ranges of this phenomenon. As the temperature is increased, the conductivity is increased and likewise the discharge rate is seen to increase; as the temperature is lowered, the rate of count rate emission decay is reduced: at normal operating temperatures the decay is not detectable using sleeves method of measurements.

It is observed that the count rate emission decay measured with an electronic scaler depends on the pressure and nature of air, the compound capacitor formed by the ionizing vessel, type of cathode, applied potential across the electrodes,

pulse height, temperature of the system, electro-conditioning of the discharge tube and lastly circuit elements etc.

These results and other results lead to the conclusion that the decay associated with the air afterglow from the container walls, and that surface state of the negate electrode accounts for the removal of electrons.

In the view of these factors, *such as observations with an ozonizer, (1) in dark and, (2) under light with d.c. excitation, (3) at different working temperatures, (4) with various gas pressures*, all of which require further study, there is no incentive to attempt a conclusion regarding the mechanism of pulsed or count rate emission decay with time or even the conditions under which pulsed emission decay exists.

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